DARPA R&D Status Report

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Program Code No.:

Contractor: General Electric Corporate Research and Development

Contract Amount: $2,582,405

Contract No.: N00014-96-C0145

Effective Date of Contract: June 26, 1996

Expiration of Contract: June 30, 2000

Principal Investigator: James Cella

Telephone No.: (518) 387-6173/(518) 387-7342

Short Title of Work: Non-toxic, Self Cleaning Silicone Foul Release Coatings

Reporting Period: April through June 1998

Description of Progress:

Task 1: Design, Synthesis and Testing of Foul Release Paints With Improved Antifouling and Release Properties

Task 1.1: Design, Synthesis and Testing of Foul Release Paints (GE-CRD)

Additional screening panels have been deployed at FIT. Concepts currently under evaluation include:
- The effect of oil incorporation into non-silicone coatings with poor foul release characteristics
- The effect of loading level of the oil on foul release properties
- The effect of molecular weight and water solubility of the oil on foul release properties

About 58 panels are deployed at MMRTS and include two panels each of the downselected compositions. Data collection continues on the first and second downselect panels at FIT, Bridger Scientific, University of Hawaii and SUNY Buffalo.

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James A Cella
Polymer Materials Laboratory
Phone: 518-387-6173
Fax: 518-387-5592

P.O. Box 8
Building K1, Room 5A64
Schenectady, NY 12301

GE Corporate Research and Development

July 8, 1998

TO: Steve Wax
Harold Guard
DCMC Hartford
Director, Naval Research Laboratory
Defense Technical Information Center

Enclosed is the DARPA R&D Status Report for April through June 1998, Contract No. N00014-96-C0145.

If you have any questions, please call me.

Sincerely,

J.A. Cella, Manager
Copolymer Technology Program

/pn
Enclosure

cc: B.J. Malloy

Task 1.1.1: Quantitative Foul Release Performance of New Materials (FIT)

Static Immersion of Test Coatings

The test coatings are applied to screening panels (4"x10") for short term evaluation, and down select panels (10"x12") for long term appraisal. A total of 143 screening panels have been exposed to barnacle fouling at the Florida Institute of Technology static immersion site since January 1997. 80 of these remain under test. A total of 39 down-select panels are currently under static immersion. Hard fouling adhesion measurements have been made on approximately 4,600 organisms on the screening panels and 2,300 organisms on the downselect panels. These include barnacles, oysters and tube worms.

Hydrodynamic Foul Release / Skin Friction Measurements

The hydrodynamic foul-release and skin friction properties of the coatings continue to be evaluated using two instrumented foils that were specifically designed and constructed to accommodate standard 10"x12" static immersion panels. Preliminary findings have been presented in a video, "Hydrodynamic Testing of Foul-Release Antifouling Coatings," April, 1998.

Task 1.1.2: Field Exposure Testing (Bridger Scientific)

Preseason inspection/testing of coatings in the first downselect matrix was performed on March 1998; data were presented and discussed in the 31 March 1998 Quarterly Report and the March program meeting, hosted by Florida Institute of Technology. The first routine inspection was performed in April at both the Brayton Point and Manchester Street Stations. At this time, all panels were photographed and assessed for fouling coverage. Panels in Series 3, 10, and 11 and one panel in Series 2 (Brayton Point) and Series 7 (Manchester Street) were removed and forwarded to Dr. Anne Meyer for post exposure analyses. These were replaced with panels in the second downselect matrix (Series 14-18). Coating formulations in both groups were inspected and tested again in May, 1998. The extend of fouling on the rest of the downselect panels is still relatively low, consisting primarily of soft fouling species. These were removed at pressures in the range of 50-100 psi (water jet). Incipient barnacle fouling was present on some panes (Series 1,2,6,7,9,12) but could also be removed at pressures between 75-100 psi. No other hard foulers were observed. Coatings in the second downselect group have been exposed approximately one month. At the time of inspection, most were covered with a light to moderate sediment/slime layer and Polydora. Incipient barnacle fouling was observed on panels in Series 14,16,17 and the front of Series 18. At this time, it is difficult to provide a distinct ranking for all coatings due to the low fouling rate and diversity (seasonal effects) and the short exposure time (second downselect matrix). Although slightly elevated pressures were required to clean panels in Series 5 and 13 compared to previous measurements, the groups continue to perform well. Coatings in Series 17 and the back of Series 18 also show favorable foul resistance and foul release properties, however, longer exposure is required in order to completely characterize these materials.

Task 1.2: Validation Testing (NSWC, University of Hawaii)

Patch tests
Patch tests have been requested on USS Nevada (SSBN 733). Two ten feet by ten feet patches will be applied during the last week in July. Inspection of the patches applied last year will occur during the third week of July. Annual evaluations based on availability are planned.

Validation Testing at the University of Hawaii

By June of 1998, for many of the experimental coatings immersed in the summer of 1997, the fouling community appeared to have reached an equilibrium characterized by high coverages of bivalve mollusks and sponges (Table 4, 5). Tubeworms (with calcareous tubes) were also abundant on some panels. Tubeworm coverage on coatings 6 and 7 was due mainly to the clonal serpulid *Salmacina dysteri*. Encrusting and arborescent bryozoans, and solitary and colonial tunicates, were much less abundant but could account for up to 10-11% of the coverage of some coatings.

All of the coatings immersed in 1997 were fouled to some extent, including BRA. Treatments 1, 2, 3, 4, 6, and 11 (front and back) were most heavily fouled with from 50-90% (mean) of their surfaces covered by macrofouling organisms. Coatings 5, 7, 8, 12, and 13 were lightly fouled.

The second set of experimental panels was immersed on April 13, 1998. After approximately 1 month of exposure, several of these panels had developed moderate encrustations of the tubeworm *Hydroides elegans*. Fouling was heaviest on coatings 14 and 16. After two months, fouling by tubeworms had decreased substantially on many panels, perhaps due to increased ship activity near the test sight disturbing the community. Levels of total fouling were similar across all the panels, although it should be noted that coating 15 supported no hard fouling.

Additional data on adhesion of *Hydroides elegans* and oysters was collected on May 27, 1998. Data were collected for the newly exposed coatings (treatments 14-18) as well as those exposed in 1997. There remained strong differences among the coating treatments for both *Hydroides elegans* and oysters). For the panels immersed in 1997, patterns in adhesion strength for both types of foulers closely matched those observed previously. Oysters had yet to settle on the new experimental coatings; however, *H. elegans* was relatively abundant. Adhesion of *Hydroides* was measured for coatings 14, 16, and 18. Adhesion strengths for coatings 14, 16, and the front of 18 were relatively high. Adhesion of *Hydroides* to the back of panel 18 was less than half that of the RTV11 on the front of this panel.

The experimental coatings immersed on April 13, 1998 were subjected to the water jet test for adhesion of slime films on May 11. Bulk slimes cleaned from all of the panels at water jet pressures of 25-50 psi, while adherent slimes could be removed from all the

panels at pressures of up to 150-200 psi (panel 14L-F). There was little in terms of adhesion of slime films to distinguish among the coatings; all of the panels save 14L were cleaned completely of slimes at relatively low pressures, generally less than 100 psi. Hard fouling present on the coatings could be removed from all panels save 16L. Soft fouling could be removed from the few coatings on which it was supported at pressures of 25 psi.

Task 2: Optimize Coating Physical and Application Properties

Task 2.1 Physical Property Optimization (GE)

Cathodic protection panels were prepared and shipped to Bridger Scientific. These formulations include a mistcoat containing control and an amended epoxy coating that requires no mistcoat. These coatings are presently being machined to allow mounting of small zincs for cathodic protection. Deployment is scheduled for early July, 1998 at Manchester Street Station.

Dry testing of the mistcoat elimination matrix of ninety-degree peel adhesion coupons with spray-applied epoxy and mistcoat was completed this month. The formulations that have been tested are Amerlock 400, Amerlock 400FD, and Seaguard 151 each with the mistcoat, and epoxy with two additives. The adhesive strength of the first system is similar to that of the mistcoat control for both Amerlock epoxies and is almost double the adhesive strength of the Seaguard 151/mistcoat control system. The addition of the second additive does not benefit adhesion in any epoxy system.

Testing this month also continues to show that spray application of the epoxy, epoxy with additives, and the mistcoat greatly improves the adhesion at the epoxy/J-501 interface. The following table illustrates the improvement for the Amerlock 400 base (data taken over six replicates):

	Avg. load (lb.) by brush application	Avg. load (lb.) by spray application
Amerlock 400 + mistcoat	3.6 ± 0.9	6.9 ± 0.4
Amerlock 400 + additive	4.9 ± 0.6	8.5 ± 0.7

Even though the peel strength of the mistcoat-free formulation is still only comparable to that of the mistcoat formulation, it is expected that improvement in adhesion performance in the field will be more due to the better control of the application window for the J-501 over the epoxy. Wet peel adhesion samples will be tested for further evaluation of these formulations.

Task 2.2.1 Cleanability of foul release coatings (SUNY Buffalo)

During this reporting quarter, surface analyses and brush abrasion testing of Downselect Set 2 was completed. Comprehensive contact angle analyses of abraded Downselect Set 2

coatings, after each stage of abrasion testing, indicated that the abraded topcoats maintained their pretest surface energetics. MAIR-infrared spectroscopy of transferable silicone residues at each stage of abrasion testing indicated that abraded topcoats on 14, 15, and 16 were similar to their pretest conditions. When topcoat 18 was abraded more, silicone could be transferred to the internal reflection prism than could be transferred from the unabraded, pretest surface of 18.

The cleanability of Downselect panels at the Medina site was evaluated in mid-June. Zebra mussels were observed on panels 6, 7 and BRA from the first downselect and 14, 15, and 16. Zebra mussels were removed by a water rinse of 1 psi from 6, 7, and 15 and incompletely removed from 14, 16 and the BRA control.

Early in April, the Bridger Scientific team removed some Downselect 1 panels from the Manchester Street and Brayton Point sites in order to make room for Downselect 2 panels. These panels are being characterized by comprehensive contact angle analyses to determine whether post exposure topcoat surface properties are different from pre-exposure properties.

Task 3: Environmental Impact and Toxicological Testing

Task 3.1: Environmental Impact (GE)

A study of the leach rates of polydimethylsiloxane (PDMS) and polydimethyldiphenylsiloxane (PDMDPS) from RTV11® has been completed. Radiometric analysis has been performed to determine the amount of oil that has leached into the water and sediment in addition to the amount of oil remaining in the RTV. After 12 months in both fresh water and salt water, <0.4% and ≤0.03% of the total ^{14}C-PDMS was detected in the water and sediment, respectively. The mass balance of ^{14}C for the salt water and fresh water systems combined was 102.23±3.99% (Table 1).

| time (months) | system | % of total ^{14}C | | | | |
		in tin rinse	in water	in sediment	in RTV	total
1	**PDMS fresh**	0.05	0.05	0.01	100.03	100.14
2	"	0.05	0.07	0.01	101.54	101.67
3	"	0.05	0.13	0.01	100.74	100.93
4	"	0.05	0.13	0.01	101.82	102.01
5	"	0.05	0.16	0.02	96.08	96.31
6	"	0.05	0.19	0.02	99.64	99.9
7	"	0.05	0.19	0.01	97.2	97.45
8	"	0.05	0.2	0.03	98.6	98.88
9	"	0.05	0.24	0.01	100.31	100.61
10	"	0.05	0.3	0.01	101.6	101.96
11	"	0.05	0.24	0.02	99.31	99.62
12	"	0.05	0.25	0.03	106	106.33
1	**PDMS marine**	0.05	0.04	0.02	95.31	95.42
2	"	0.05	0.07	0.01	105.53	105.66
3	"	0.05	0.12	0.02	103.3	103.49
4	"	0.05	0.13	0.03	109.64	109.85
5	"	0.05	0.15	0.01	104.91	105.12
6	"	0.05	0.17	0.01	102.89	103.12
7	"	0.05	0.16	0.02	101.29	101.52
8	"	0.05	0.18	0.01	98.89	99.13
9	"	0.05	0.19	0.02	99.7	99.96
10	"	0.05	0.23	0.02	106.92	107.22
11	"	0.05	0.24	0.03	105.86	106.18
12	"	0.05	0.36	0.03	110.53	110.97
					average	102.23
					std. dev.	3.99

Table 1 *mass balance of ^{14}C-polydimethylsiloxane (PDMS)*

After 12 months in both fresh water and salt water, <1.1% and ≤0.07% of the total ^{14}C-PDMDPS was detected in the water and sediment, respectively. The mass balance of ^{14}C for the salt water and fresh water systems combined was 100.65+6.50% (Table 2).

time (months)	system	% of total ^{14}C in tin rinse	in water	in sediment	in RTV	total
1	**SF1154 fresh**	0.4	0.11	0.02	103.49	104.02
2	"	0.4	0.15	0.02	94.84	95.41
3	"	0.4	0.19	0.03	102.52	103.14
4	"	0.4	0.34	0.05	94.11	94.90
5	"	0.4	0.08	0.05	89.7	90.23
6		0.4	0.06	0.05	100.26	100.77
7		0.4	0.64	0.06	98.37	99.47
8		0.4	0.33	0.06	99.69	100.48
9		0.4	0.62	0.06	95.41	96.49
10		0.4	0.25	0.08	95.02	95.75
11		0.4	1.01	0.08	88.61	90.10
12		0.4	1.03	0.06	96.6	98.09
1	**SF1154 marine**	0.4	0.09	0.04	103.98	104.51
2	"	0.4	0.08	0.03	92.36	92.87
3	"	0.4	0.11	0.03	102.94	103.48
4	"	0.4	0.11	0.02	105.02	105.55
5		0.4	0.07	0.05	101.97	102.49
6		0.4	0.2	0.05	104.55	105.20
7		0.4	0.09	0.06	93.21	93.76
8		0.4	0.05	0.03	107.65	108.13
9		0.4	0.04	0.06	98.3	98.80
10		0.4	0.1	0.06	114.3	114.86
11		0.4	0.15	0.08	102.5	103.13
12		0.4	0.97	0.07	112.6	114.04
					average	**100.65**
					std. dev.	**6.50**

Table 2 *mass balance of ^{14}C-poly(dimethyldiphenyl)siloxane (PDMDPS)*

Task 3.2: Toxicological Studies (NSWC, NCCOSC)

This quarter's activities focused on conducting toxicity tests on 3 new coatings sent to SPAWAR Systems Center for evaluation. All 3 coating films were tested for toxicity with leachates made from the films. These tests included the 4 day Mysid shrimp survival

test, the 4 day fish test and the 4 day diatom fluorescence test. Leachates from the coatings have been collected and will be analyzed for TBT. The most toxic coating to the shrimp and the fish was the RTV11 control.

Task 4. Large Scale Validation (GE)

An intermediate-scale real-world application, performed in May at FIT, was used for additional evaluation of the fouling-release properties of one of the best-performing topcoats, and for evaluation of the performance of the mistcoat-containing Duplex system and the new mistcoat-free coating system. The starboard side of the 21' fiberglass boat was coated with the mistcoat-containing Duplex system (as a control), and the port side was coated with amended Amerlock 400 epoxy. The entire boat was finished with a top-performing RTV11 + oil fouling release topcoat.

Sandblasting of the boat hull to remove the existing coatings pitted the surface of the fiberglass. To ensure complete coverage, two base coats of unaltered epoxy were applied to the entire hull. The final surface is not as smooth as those seen in other applications.

The application took place inside a building owned by FIT. Before the application of each epoxy layer, the entire hull was wiped down with naphtha to remove dust and moisture. The first epoxy base coat, ivory Amerlock 400, was applied on the first day and allowed to cure overnight before application of the second coat, pearl gray Amerlock 400, on the second day. The mistcoat, experimental epoxy, J-501, and RTV11 were applied on the third day. A curtain was used to separate the mistcoat and experimental epoxy but was removed to apply J-501 and RTV11 over the entire surface of the hull. Both the amended Amerlock 400 and the J-501 + 10% SF69 sprayed easily. The GE repair package with J-501 and RTV11 was used to repair the block shift patches the fourth day. The system was allowed to cure for one week before the boat is launched. Barnacle adhesion measurements, drag evaluations, hydrodynamic testing, and power trials will be performed by FIT to evaluate the coating system's adhesion and fouling-release properties. Power trials are expected to take place in September or October 1998.

Change in Key Personnel:

None

Summary of Substantive Information Derived from Special Events

Judy Stein and Jim Cella met with personnel at NAVSEA O3M and presented updates of the ESTCP and DARPA programs. Procedure for qualification was also discussed.

A copy of a publication submitted to the American Chemical Society is appended.

Problems Encountered and/or Anticipated:

None

Action Required by the Government:

None

Fiscal Status:
Project Cost: $1,152,000
Cost Share: (281,601)
Net to ONR/DARPA: $ 870,399

Advances in NonToxic Silicone Biofouling Release Coatings

Tim Burnell[1], John Carpenter[1], Kathryn Truby[1], Judy Serth-Guzzo[1],
Judith Stein[1], and Deborah Wiebe[2]

[1]GE Corporate Research and Development
Niskayuna, NY 12301
[2]Bridger Scientific, Inc.
Sandwich, MA 02532

Abstract: In this paper, we report two methods to control oil depletion from silicone foul release coatings: ablative networks and tethered incompatible oils. The synthesis of ablative and tethered diphenyldimethylsiloxane oils, the incorporation of such oils into the silicone room temperature vulcanized (RTV) network and the foul release properties of RTV coatings containing the ablative and tethered oils are discussed. The residence time of radiolabeled diphenyldimethylsiloxane oils in silicone RTV topcoats is also addressed. Synthesis of the radiolabeled diphenyldimethylsiloxane oil and incorporation of the radiolabeled oil into the silicone network are discussed. In addition, the environmental partitioning of the radiolabeled oils in both freshwater and marine systems is presented with the material balance.

Introduction

Marine biofouling is a significant problem for ships and other structures submerged in a marine environment *(1)*. Both calcareous and non-calcareous fouling types present problems. Calcareous organisms, or "hard" foulers, are found in both marine and freshwater environments. Those found in marine water include barnacles, blue mussels, and encrusting bryazoans; those found in freshwater include zebra muscles. Examples of non-calcareous organisms, or "soft" foulers, are algae, slime, hydroids and tunicates. Barnacles are the biofouling organism of interest for this paper.

For ship owners, the fouling of the ship hull has many detrimental effects. Both soft and hard fouling leads to increased drag on the ship which decreases both the speed and fuel efficiency of the vessel, and consequently leads to an increase in operating expenses *(1)*. It has been reported that for oceangoing freighters, a 20% increase in fuel costs, or ~ $1 MM per year could be anticipated *(2)*.

Traditional antifouling coatings, such as paints containing heavy metals, organic biocides and tin or copper ablative coatings, are highly effective at preventing biofouling. Such coatings release toxic substances into the water adjacent to the coating surface, thereby killing the biofouling before strong attachment can occur (3). Consequently, antifouling coatings provide an environmental risk to marine organisms since they release toxins into the environment. Not surprisingly, the use of cupric oxide in paints is expected to be limited in the near future due to environmental concerns and triorganotin species, also very effective, are prohibited for use by the U.S. Navy.

For these reasons, much interest has evolved in nontoxic foul-release coatings, such as silicones (4). These coatings inhibit the strong attachment of marine organisms via an "easy release" mechanism. Several desirable properties of silicone coatings minimize the adhesive strength of biofouling attachment and once fouling does occur, it can be removed easily by physical processes such as water pressure washing or gentle scrubbing. The easy release properties of silicones have been demonstrated empirically to be related to the glass transition temperature (Tg) and surface energy of the silicone coatings. The low Tg (-127°C) is attributed to the flexible siloxane backbone, which gives it its very high molecular mobility, even as a high molecular weight elastomer. Thus, coatings based on polymers with high Tg's tend to have poor fouling release, even at very low surface energy values. For example, Teflon, $-(CF_2CF_2)_n-$ or poly(tetrafluouroethylene), has a Tg of 130°C due to its rigid backbone and exhibits poor foul release properties. Silicones also have a critical surface tension that coincides with the minimum of a plot of relative attachment versus surface free energy (5). GE's foul release coatings, described below, exhibit both low Tg and low surface free energy.

GE foul release coatings are comprised of a silicone topcoat and a silicone oil additive, typically at 10 or 20 weight percent. The silicone topcoat, RTV11®, is a room temperature condensation moisture cure system, which contains a silanol terminated polydimethylsiloxane (PDMS), $CaCO_3$ filler, tetraethoxyorthosilicate (TEOS) crosslinker and dibutyltin dilaurate, a Sn(IV) catalyst. The chemistry of this system is shown below in Figure 1.

Barnacle adhesion testing is a technique used to measure the foul release performance of foul release coatings and is performed at static exposure sites such as the Indian River Lagoon in Melbourne, Florida. Barnacle adhesion testing is performed using a force gauge according to ASTM D5618-94. This technique measures the shear force required to remove barnacles adhered to the surface of a coating. Using barnacle adhesion data, it has been shown empirically that improvements in foul release is observed in coatings containing oils. First demonstrated by International Paint in the 1970's (6), the Navy and then GE began incorporating oils into their foul release topcoats in the late 1980's and early 1990's, respectively. As shown below in Figure 2, RTV11® exhibits superior barnacle adhesion relative to an epoxy control; however, RTV11® containing 10% free diphenyldimethyl siloxane oil performs superior to both the epoxy control and RTV11®. Since free oils in the silicone coating demonstrate improved foul release and since it is desirable to maximize the lifetime of the oil in the topcoat for maximum foul release performance, the following questions need to be addressed. Does oil need to be at the surface? Can oil diffusion from the matrix be controlled by attaching either ablative or tethered oils into the silicone topcoat?
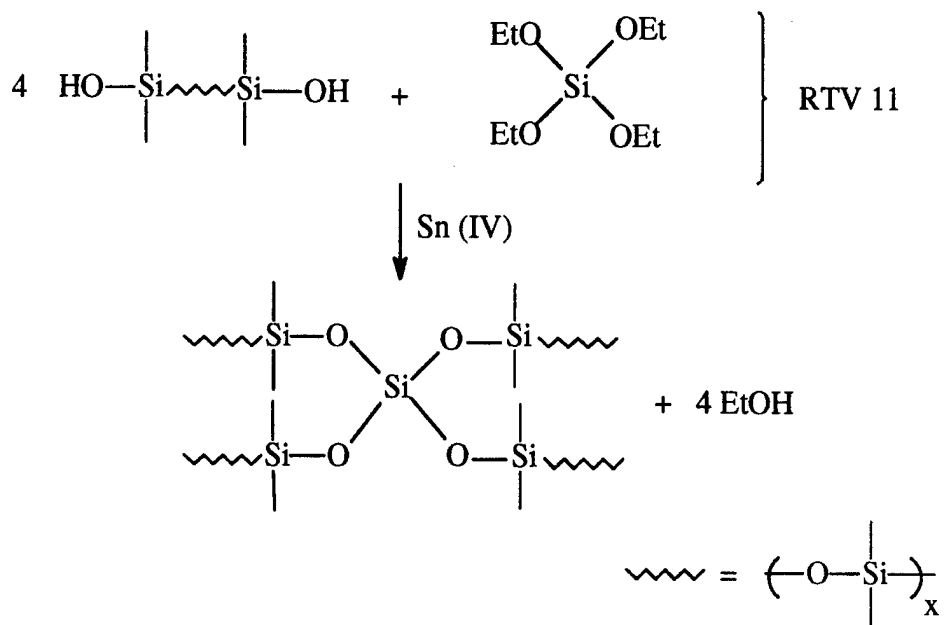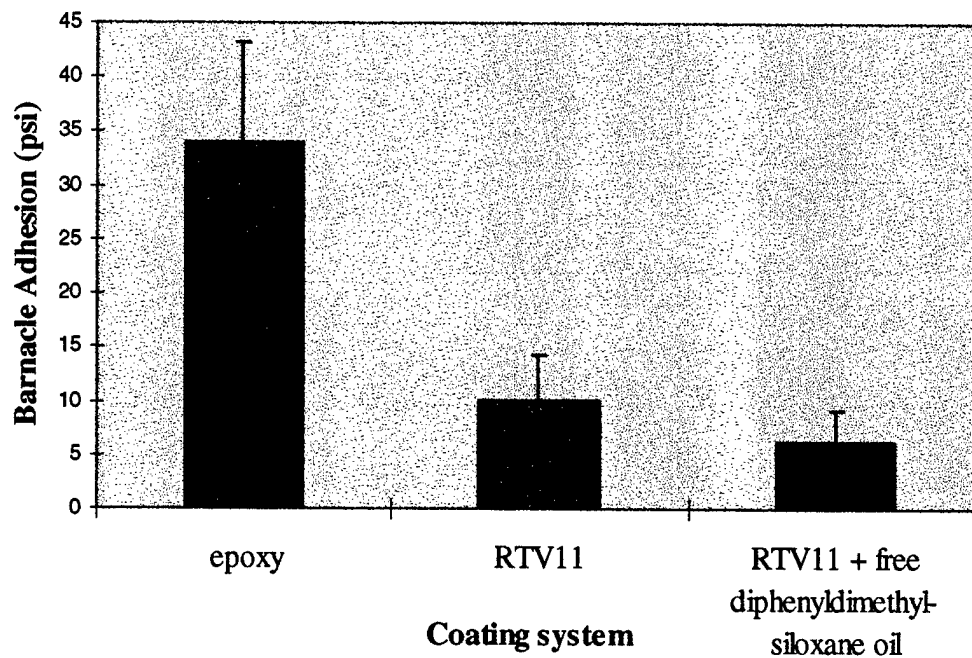
Figure 1. RTV11® Chemistry

Figure 2. Barnacle Adhesion Data for Various Coatings

Mechanisms for Oil Retention in RTV11 Topcoat: Ablative Networks and Tethered Incompatible Oils
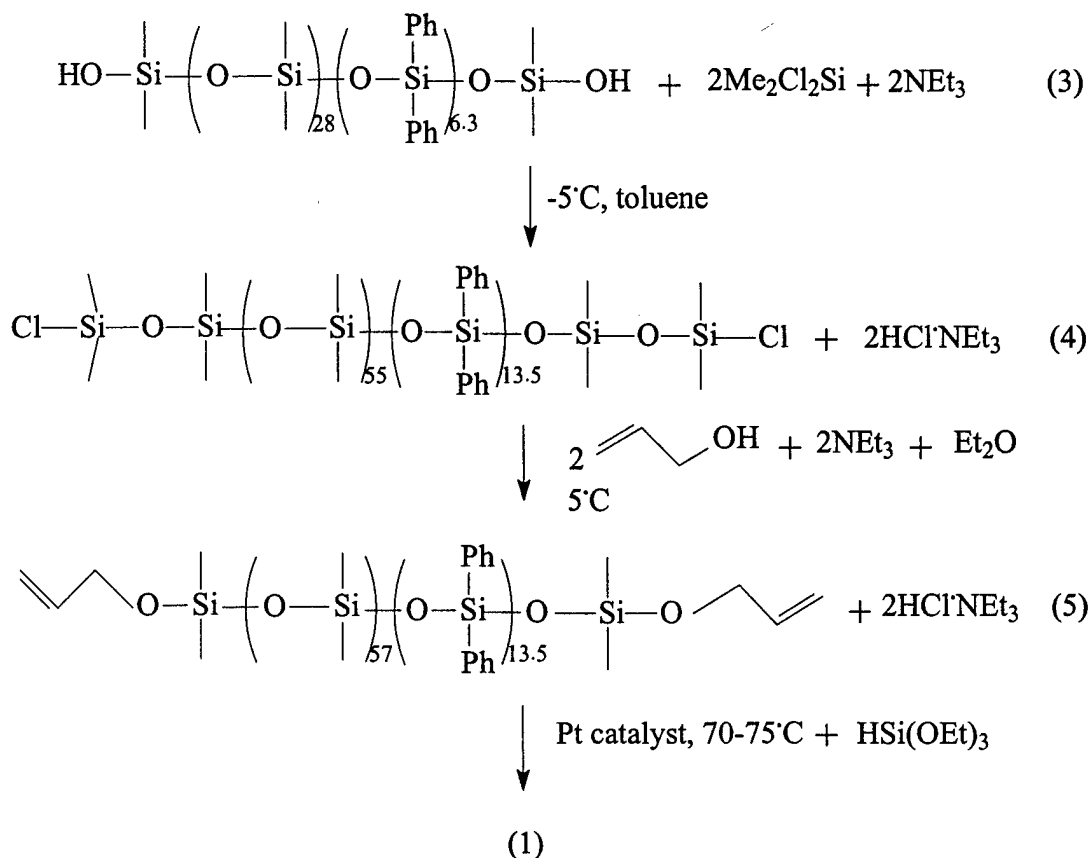
The incorporation of ablative and tethered oils into the silicone topcoat of fouling release coatings is a desirable mechanism for slow, controlled release of the silicone oil from the RTV topcoat. Once incorporated into the silicone network, the hydrolytically unstable Si-O-C bond in the ablative oil (Figure 3) should slowly degrade in water. Conversely, the tethered oil is chemically bonded into the silicone network and one end (the non-miscible portion) should phase separate to the surface of the PDMS. Both ablative and tethered oils contain diphenyldimethylsiloxane functionality, based on previous studies of the free oil. The approach was to synthesize both ablative and tethered diphenyldimethylsiloxane copolymers, incorporate the copolymers into the RTV topcoat and then measure the foul release performance of the coatings. Both oils are shown below in Figure 3.

Figure 3. Summary of Ablative (1) and Tethered (2) Diphenyldimethylsiloxane Oils
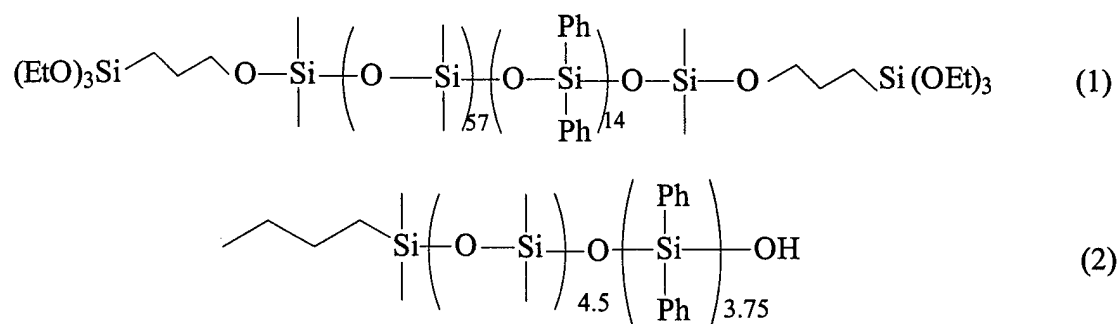
The synthesis of the ablative diphenyldimethylsiloxane oil involved three steps, shown below in Figure 4. A silanol terminated diphenyldimethylsiloxane copolymer (3) containing 16 mole % diphenylsiloxane was reacted with dimethyldichorosilane at -5°C in the presence of triethylamine to give the bis-chlorosilane terminated derivative (4). The chlorosilane derivative was subsequently reacted with allyl alcohol and triethylamine to yield the bis-allyl terminated diphenylmethylsiloxane (5). Hydrosilyation with triethoxysilane and Karstedt's catalyst gave the product, bis-triethoxy terminated diphenyldimethylsiloxane (1). Note some chain extension was observed in (4), where the molecular weight doubled from approximately 3,300 to 7,000.

Figure 4. Synthesis of Ablative Diphenyldimethylsiloxane Oil

$$\text{HO}-\underset{|}{\overset{|}{\text{Si}}}-\left(\text{O}-\underset{|}{\overset{|}{\text{Si}}}\right)_{28}\left(\text{O}-\underset{\overset{|}{\text{Ph}}}{\overset{\text{Ph}}{\text{Si}}}\right)_{6.3}\text{O}-\underset{|}{\overset{|}{\text{Si}}}-\text{OH} \;+\; 2\text{Me}_2\text{Cl}_2\text{Si} + 2\text{NEt}_3 \qquad (3)$$

$$\downarrow \text{ -5°C, toluene}$$

$$\text{Cl}-\underset{/}{\overset{\backslash}{\text{Si}}}-\text{O}-\underset{|}{\overset{|}{\text{Si}}}-\left(\text{O}-\underset{|}{\overset{|}{\text{Si}}}\right)_{55}\left(\text{O}-\underset{\overset{|}{\text{Ph}}}{\overset{\text{Ph}}{\text{Si}}}\right)_{13.5}\text{O}-\underset{|}{\overset{|}{\text{Si}}}-\text{O}-\underset{|}{\overset{|}{\text{Si}}}-\text{Cl} \;+\; 2\text{HCl·NEt}_3 \quad (4)$$

$$\downarrow \;\; 2\; \diagup\!\!\diagup\!\diagdown\text{OH} + 2\text{NEt}_3 + \text{Et}_2\text{O}$$
$$5°C$$

$$\diagdown\!\!\diagdown\text{O}-\underset{|}{\overset{|}{\text{Si}}}-\left(\text{O}-\underset{|}{\overset{|}{\text{Si}}}\right)_{57}\left(\text{O}-\underset{\overset{|}{\text{Ph}}}{\overset{\text{Ph}}{\text{Si}}}\right)_{13.5}\text{O}-\underset{|}{\overset{|}{\text{Si}}}-\text{O}\diagup\!\!\diagup\!\diagdown \;+\; 2\text{HCl·NEt}_3 \quad (5)$$

$$\downarrow \text{ Pt catalyst, 70-75°C} + \text{HSi(OEt)}_3$$

$$(1)$$

The tethered diphenyldimethylsiloxane oil was prepared by a kinetically controlled anionic ring opening polymerization of hexamethylcyclotrisiloxane (D$_3$) and hexaphenylcyclotrisiloxane (D$_3^{Ph}$) in the presence of n-BuLi (Figure 5) *(7)*. Once the lithium salt of D$_3$ and D$_3^{Ph}$ (6) was formed in a two step process, it was then quenched with water to give a silanol terminated diphenyldimethylsiloxane product (2).
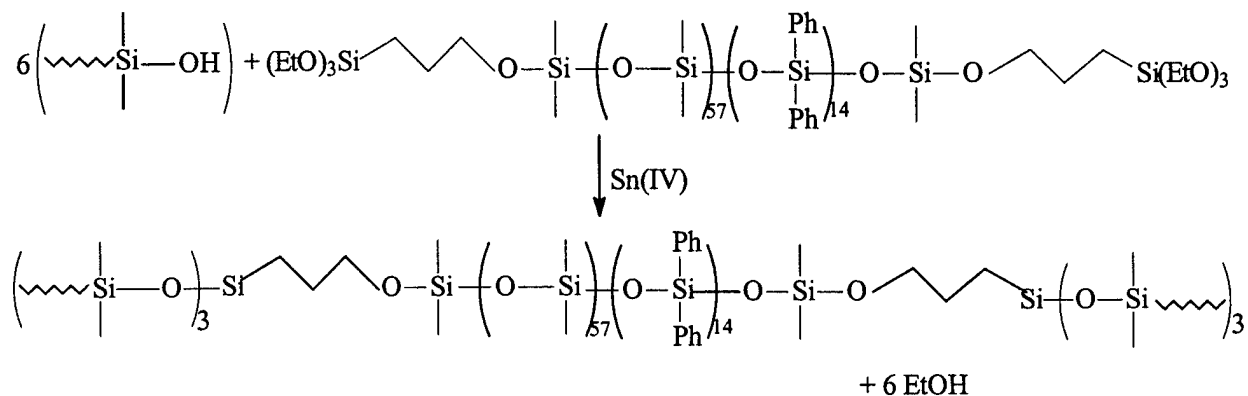
Figure 5. Synthesis of Tethered Diphenyldimethylsiloxane Oil

$$1.5\,\text{D}_3 + 1.25\,\text{D}_3^{Ph} + \text{BuLi} \xrightarrow[\text{toluene}]{\text{THF}} \diagup\!\!\diagdown\!\!\diagup\!\!\diagdown\underset{|}{\overset{|}{\text{Si}}}\left(\text{O}-\underset{|}{\overset{|}{\text{Si}}}\right)_{4.5}\text{O}\left(\underset{\overset{|}{\text{Ph}}}{\overset{\text{Ph}}{\text{Si}}}\right)_{3.75}\text{O}^-\text{Li}^+ \quad (6)$$

$$\swarrow \text{ HCl/H}_2\text{O}$$

$$\diagup\!\!\diagdown\!\!\diagup\!\!\diagdown\underset{|}{\overset{|}{\text{Si}}}\left(\text{O}-\underset{|}{\overset{|}{\text{Si}}}\right)_{4.5}\text{O}\left(\underset{\overset{|}{\text{Ph}}}{\overset{\text{Ph}}{\text{Si}}}\right)_{3.75}\text{OH} \qquad (2)$$
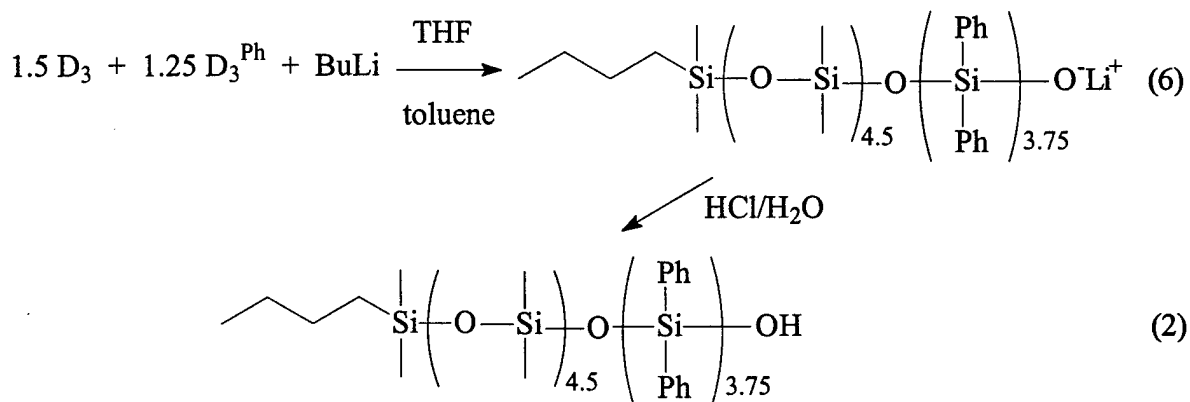
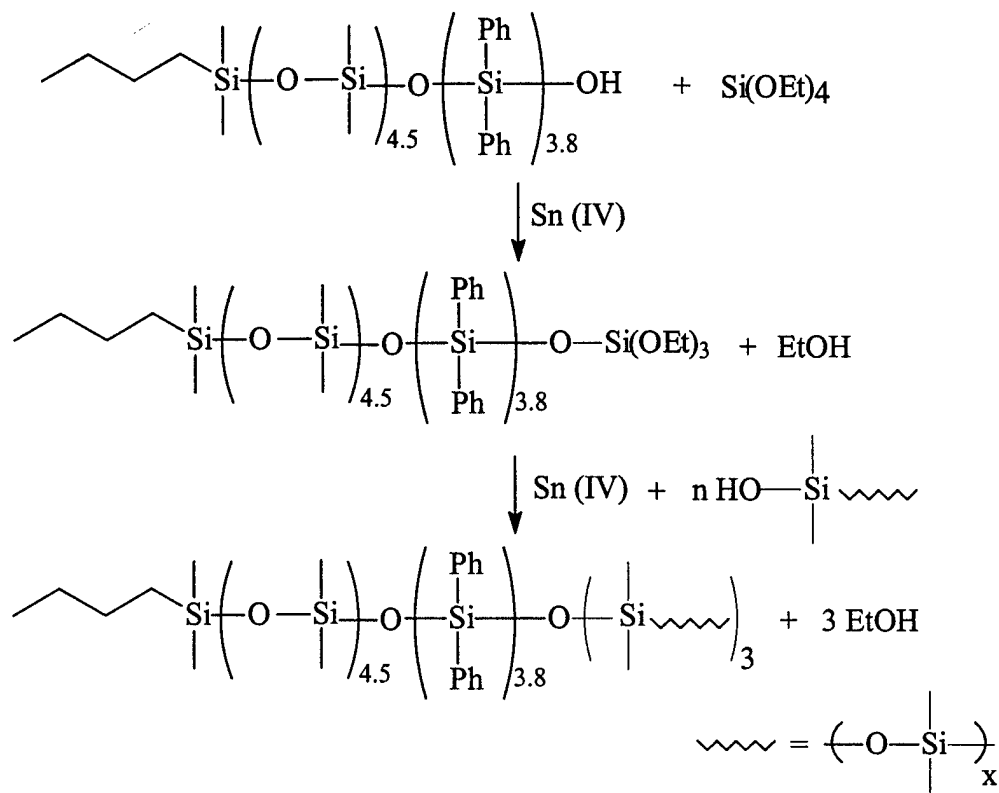## Incorporation of Ablative and Tethered Oils into Silicone Network

The ablative diphenyldimethylsiloxane copolymer was incorporated at 10 wt % into the PDMS network (Figure 6). The bis-triethoxysiloxane end groups of (1) condense with the silanol terminated PDMS in the presence of Sn(IV) to give a crosslinked network containing the hydrolytically unstable Si-O-C moiety.

Figure 6. Incorporation of Ablative Diphenyldimethylsiloxane Oil into RTV Network

$$6\left(\text{\textasciitilde\textasciitilde Si—OH}\right) + (\text{EtO})_3\text{Si}\diagdown\diagup\text{O—Si}\left(\text{O—Si}\right)_{57}\left(\text{O—Si}^{Ph}_{Ph}\right)_{14}\text{O—Si—O}\diagup\diagdown\text{Si(EtO)}_3$$

$$\downarrow \text{Sn(IV)}$$

$$\left(\text{\textasciitilde\textasciitilde Si—O}\right)_3\text{Si}\diagdown\diagup\text{O—Si}\left(\text{O—Si}\right)_{57}\left(\text{O—Si}^{Ph}_{Ph}\right)_{14}\text{O—Si—O}\diagup\diagdown\text{Si}\left(\text{O—Si}\text{\textasciitilde\textasciitilde}\right)_3$$

$$+\ 6\ \text{EtOH}$$

Likewise, the tethered diphenyldimethylsiloxane oil was also incorporated at 10 wt % into the PDMS network (Figure 7). The silanol endgroups of (2) condense with TEOS in the presence of Sn(IV) to give the triethoxy-terminated copolymer, which subsequently condense with the silanol-terminated RTV11® to form a crosslinked network. The incompatible butyl-terminated diphenyldimethyl fragment should phase separate to the surface of the PDMS network

Figure 7. Incorporation of Tethered Diphenyldimethylsiloxane Oil into RTV Network

$$\text{(structure)} \quad \text{Si}\!\!\left(\!\!\text{O—Si}\!\!\right)_{4.5}\!\!\text{O}\!\!\left(\!\!\begin{array}{c}\text{Ph}\\\text{Si}\\\text{Ph}\end{array}\!\!\right)_{3.8}\!\!\text{OH} \quad + \quad \text{Si(OEt)}_4$$

$$\downarrow \text{Sn (IV)}$$

$$\text{(structure)} \quad \text{Si}\!\!\left(\!\!\text{O—Si}\!\!\right)_{4.5}\!\!\text{O}\!\!\left(\!\!\begin{array}{c}\text{Ph}\\\text{Si}\\\text{Ph}\end{array}\!\!\right)_{3.8}\!\!\text{O—Si(OEt)}_3 \quad + \quad \text{EtOH}$$

$$\downarrow \text{Sn (IV)} \; + \; n\, \text{HO—Si} \text{\textbackslash\textbackslash\textbackslash}$$

$$\text{(structure)} \quad \text{Si}\!\!\left(\!\!\text{O—Si}\!\!\right)_{4.5}\!\!\text{O}\!\!\left(\!\!\begin{array}{c}\text{Ph}\\\text{Si}\\\text{Ph}\end{array}\!\!\right)_{3.8}\!\!\text{O}\!\!\left(\!\!\text{Si}\text{\textbackslash\textbackslash\textbackslash}\!\!\right)_3 \quad + \quad 3 \text{ EtOH}$$

$$\text{\textbackslash\textbackslash\textbackslash} = \left(\!\!\text{O—Si}\!\!\right)_x$$

Foul Release Performance of Ablative and Tethered Oils

RTV topcoats containing either the ablative or tethered diphenyldimethylsiloxane copolymers were applied to steel panels previously coated with the epoxy and a tie layer developed at NRL *(8)*. After the panels were allowed to cure for one week, they were deployed at both northeast and southeast static test sites for 9 months. Controls of RTV11[®] and RTV11[®] containing 10% free diphenyldimethyl siloxane oil were also immersed in these marine environments. The overall fouling coverage was recorded for the northeast site and barnacle adhesion values were measured for the southeast site. Results are shown below in Figures 8 and 9.

Figure 8. Foul Release Performance of Ablative Diphenyldimethylsiloxane Oil

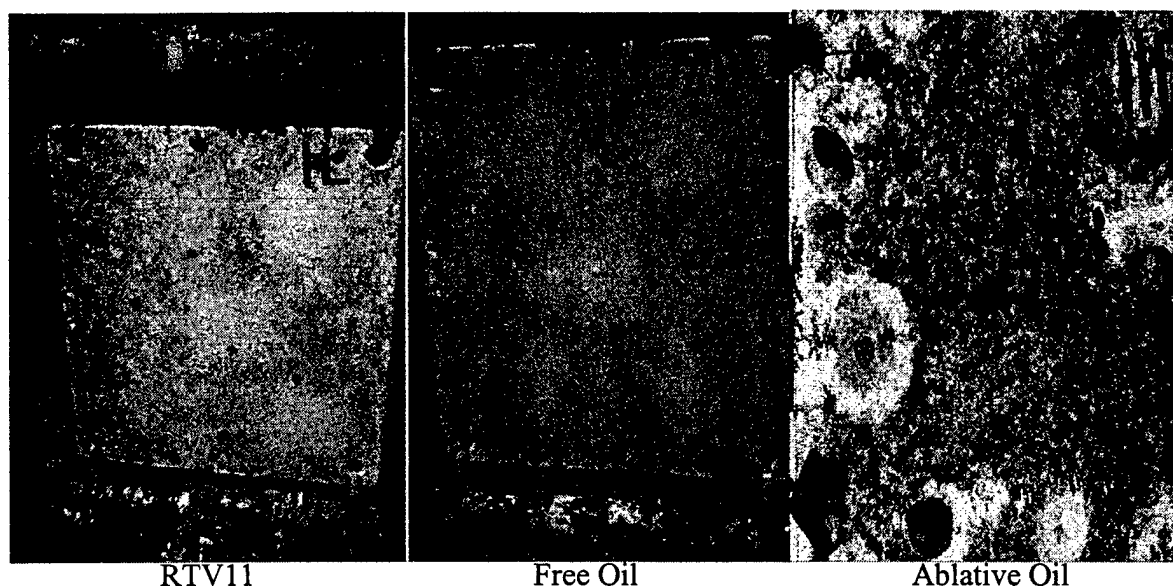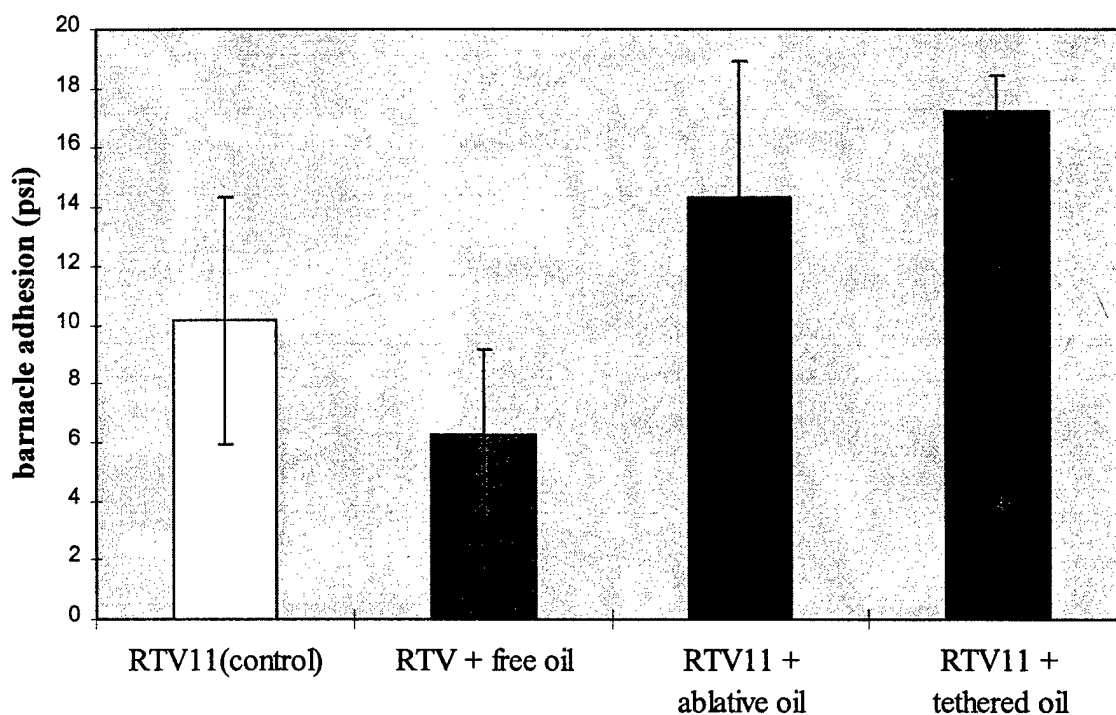RTV11   Free Oil   Ablative Oil

Figure 9. Foul Release Performance of Ablative and Tethered Oils

From Figure 8, we observe that the ablative oil, which is chemically bound to the PDMS topcoat, provides inferior antifouling performance compared to both the free diphenyldimethylsiloxane oil in RTV11® and the RTV11® control. Likewise, the barnacle adhesion data in Figure 9 suggests the coatings containing the tethered and the ablative oils performed poorly relative to the controls (RTV11® and RTV11® + free oil). From these results, we can conclude that free oil

is necessary in the silicone coating for optimal foul release performance. However, it is desirable to also understand the rate of oil depletion of silicone foul release coatings containing free oil since depletion of the oil is anticipated to adversely affect biofouling release performance. Thus, does the free oil deplete from the matrix and decrease foul release performance of these coatings?

^{14}C Radiolabeled Oil Study

The leach rate of silicone oil additives from the silicone topcoat was readily determined using ^{14}C radiolabeled oils in both fresh and marine water systems (9). Use of radiolabeled oils simplifies the study of their environmental partitioning, since each component of the matrix can be easily analyzed and quantified using radiometric detection. The approach was to synthesize ^{14}C radiolabeled polydiphenyldimethylsiloxane oil which is similar in composition to that used in determination of barnacle adhesion measurements (see Figure 2). Next, the ^{14}C oil was added to RTV11®, catalyzed and applied to metal coupons which were subsequently suspended in fresh and salt water fish tanks. Coupons, soil and sediment were analyzed monthly for one year for mass balance determination.

The radiolabeled ^{14}C polydiphenyldimethylsiloxane oil was synthesized as shown in Figure 10. The precursor, ^{14}C labeled octamethylcyclotetrasiloxane (D$_4$), was first prepared by reaction of ^{14}C-labeled methyl Grignard reagent with tetrachlorotetramethylcyclotetrasiloxane. The precursor, ^{14}C-D$_4$, was then equilibrated with and dodecamethylpentasiloxane in the presence of potassium trimethylsilanolate catalyst. Analysis of the resultant oil by ^{29}Si NMR revealed a dimethylsiloxy:diphenylsiloxy ratio of 46.7:53.3 (wt:wt) with 10.5 wt% trimethoxysiloxy endroups.

Figure 10. Synthesis of ^{14}C-labeled Polydiphenyldimethylsiloxane
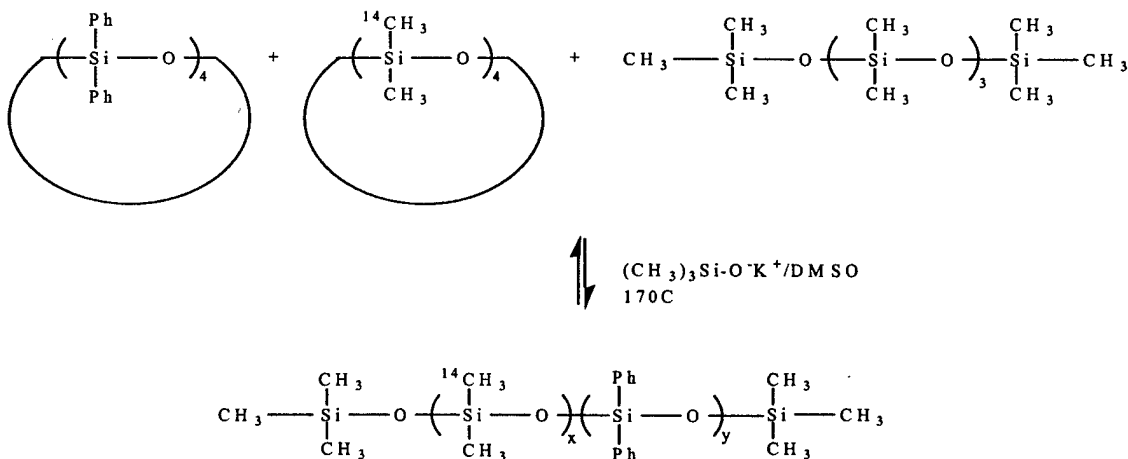
Results of Radiolabeled Studies

After 8 months in the fresh water system, <0.4% and <0.07% of the total ^{14}C-labeled oil were detected in the water and sediment, respectively. Similarly, after 8 months in the marine system,

<0.06% and <0.04% of the total ^{14}C-labeled oil were detected in the water and sediment, respectively. Mass balance data (Table I and II) reveal that, on average, >99% of the theoretical amount of ^{14}C-labeled oil remained in the silicone topcoat. Thus, levels of ^{14}C in the water are only slightly higher than background levels. Also, note the total % of ^{14}C-labeled oil does not consistently sum to 100% each month. This is probably because the oil was not uniformly dispersed in the PDMS network due to its immiscibility.

Table I. Material Balance for Fresh Water

time (months)	% of total ^{14}C				
	in Sn rinse	in water	in sediment	in RTV	total
1	0.4	0.11	0.02	103.49	104.02
2	0.4	0.15	0.02	94.84	95.41
3	0.4	0.19	0.03	102.52	103.14
4	0.4	0.34	0.05	94.11	94.9
5	0.4	0.08	0.05	89.7	90.23
6	0.4	0.06	0.05	100.26	100.77
7	0.4	0.64	0.06	98.37	99.47
8	0.4	0.33	0.06	99.69	100.48
Mean		0.238	0.043	97.87	98.55
std dev				4.67	4.67

Table II. Material Balance for Marine Water System

time (months)	% of total ^{14}C				
	in Sn rinse	in water	in sediment	in RTV	total
1	0.4	0.09	0.04	103.98	104.51
2	0.4	0.08	0.03	92.36	92.87
3	0.4	0.11	0.03	102.94	103.48
4	0.4	0.11	0.02	105.02	105.55
5	0.4	0.07	0.05	101.97	102.49
6	0.4	0.2	0.05	104.55	105.2
7	0.4	0.09	0.06	93.21	93.76
8	0.4	0.05	0.03	107.65	108.13
Mean		0.1	0.039	101.46	102
std dev				5.61	5.61

Conclusions

From the foul release results of the ablative and tethered oils, we can conclude that free oil is necessary in the silicone coating for optimal foul release performance. In addition, the radiolabeled studies indicate that the free diphenyldimethysiloxane oil leaches very slowly from the RTV11®. Thus, if loss of biofouling release performance was to be observed over time in these silicone paint systems, it could not be explained by loss of silicone oil from the topcoat. Retention of oils by the silicone topcoat also suggests that silicone paint systems of this type should not result in significant accumulation of silicone oils in marine and fresh water environments.

Experimental

All reagents were purified and/or dried over sieves prior to use. Triethylamine was distilled from CaH_2 and stored over 3Å molecular sieves (55 ppm H_2O). Toluene was distilled from sodium/benzophenone. Dimethyldichlorosilane was distilled under nitrogen and stored over 3Å molecular sieves. Diethylether was stored over molecular sieves for several days (16 ppm H_2O). PDS-1615 was obtained from Gelest and heated to 60°C under high vacuum with stirring for 1 hour to remove residual water. Allyl alcohol was dried over crushed $CaSO_4$ and 3Å molecular sieves (140 ppm H_2O). Standard schlenk techniques and a nitrogen atmosphere were used.

Synthesis of bis-chlorosilane-terminated diphenylsiloxanedimethylsiloxane (4)

A 500 mL 3-neck round bottom flask was dried overnight and fitted with an overhead stirrer and a 250 mL pressure equalizing addition funnel. $MeSi_2Cl_2$ (29.0 g, 225 mmol) was added to the flask via cannula. Upon addition of NEt_3 (12.54 mL, 90 mmol) via syringe to the system, a cloudy white gas and a white precipitate formed. An ice bath (5°C) was immediately placed under the round bottom flask and a 50 wt % solution of PDS-1615 (silanol-terminated diphenylsiloxane-dimethylsiloxane copolymer) in toluene was added drop wise from the pressure equalizing addition funnel. The temperature of the ice bath was dropped to -5°C. The silanol-terminated solution was added over 120 minutes and a cloudy white precipitate formed ($HCl \cdot NEt_3$). The reaction mixture was filtered two times and residual $MeSi_2Cl_2$ and toluene were removed by distillation. A clear viscous liquid (118.7 g, 35 mmol) was obtained and characterized by ^{1}H and ^{29}Si NMR. The ^{1}H NMR was identical to the starting material, silanol terminated diphenyldimethylsiloxane copolymer, except the disappearance of the -OH proton was observed and appearance of methyl protons adjacent to the chlorosilane were observed. ^{1}H NMR: Si-Cl: 0.3 ppm, 12 H, s; Aryl H (Ph): average δ 7.6 ppm, m, 54H; Aryl H (Ph): average δ 7.2 ppm, m, 81 H; Si-Me$_2$ (D groups): multitude of singlets at 0-0.5 ppm (342 H).

Synthesis of bis-allyl-terminated diphenyldimethylsiloxane (5)

A 1 L 3-neck round bottom flask was fitted with an overhead stirrer and a 250 mL pressure equalizing addition funnel containing the chlorosilane-terminated diphenylsiloxane dimethylsiloxane copolymer (118.0 g, 35 mmol). Allyl alcohol (7.14 mL, 105 mmol) and

triethylamine (9.76 mL, 35 mmol) were added via syringe to the 1 L flask followed by 500 mL of diethyl ether. The chlorosilane was added drop wise to the ether solution at 5°C over 90 minutes. The solution was allowed to stir an additional 15 min. and was then filtered to remove HCl·NEt$_3$. The organic layer washed with acid, water, dried over MgSO$_4$followed by distillation of the ether at 30°C. A clear viscous liquid (116 g) resulted with a molecular weight of 7,000. By ^{1}H NMR NMR, disappearance of the methyl protons adjacent to the chlorosilane and appearance of the allyl protons were observed. ^{1}H NMR: terminal CH$_2$ of allyl: 5.1 ppm, d, 4H; center CH of allyl: 5.9 ppm, ddt, 2H; CH$_2$-O: 4.2 ppm, m, 4 H. Aryl H (Ph): average δ 7.6 ppm, m, 54H; Aryl H (Ph): average δ 7.2 ppm, m, 81 H; Si-Me$_2$ (D groups): multitude of singlets at 0-0.5 ppm (354 H).

Synthesis of bis-triethoxy-terminated diphenyldimethylsiloxane (1)

To a 250 mL 3-neck round bottom flask fitted with an overhead stirrer, 5 wt% Karstedt's catalyst in xylenes (0.28 mL, 100 ppm H$_2$O) and triethoxysilane, which had been distilled under nitrogen (6.12 mL, 33.14 mmol), was added. The solution turned brown upon which ~ 5 ml of the bis-allyl copolymer was added directly with stirring. The remaining bis-allyl copolymer was added drop wise at 70-75°C over 60 minutes. ^{1}H NMR revealed disappearance of the allyl protons and appearance of the propyl and the ethoxy protons. ^{1}H NMR: propyl CH$_2$-Si 0.6 ppm, t, 4H; propyl -CH$_2$-: 1.6 ppm, m, 4H; CH$_2$-O: ~1.8 ppm, t, 4H; Aryl H (Ph): average δ 7.6 ppm, m, 54H; Aryl H (Ph): average δ 7.2 ppm, m, 81 H; Si-Me$_2$ (D groups): multitude of singlets at 0-0.5 ppm (354 H).

Synthesis of Tethered Diphenyldimethylsiloxane Oil (2)

To a 250 mL round bottom flask, 13.6g of D$_3$Ph, 30g of D$_3$, 30 mL of THF and 100 mL of toluene was allowed to stir overnight. The reaction mixture was cooled to 0°C in and 27 mL of n-BuLi (1.6M) was added. The mixture was then heated to 60°C for 6 hrs and follow by GC until no n-BuLi remained. Ether was added and then the lithium salt was quenched with water/HCl until neutral. The aqueous fraction was extracted 3 times with ether and then washed with water/NaCl. The organic fraction was then dried over Na$_2$SO$_4$ and then stripped at 150°C and 2 mmHg to remove low boiling volatiles. ^{1}HNMR: CH$_3$-CH$_2$- 2.7 ppm, t, 3 H; -CH$_2$-CH$_2$-: 1.2 ppm, m, 4H; CH$_2$-Si: 0.5 ppm, t, 2 H; OH: 2.5 ppm, broad s, 1H; Aryl H (Ph): average δ 7.6 ppm, m, 15 H; Aryl H (Ph): average δ 7.2 ppm, m, 22.5 H; Si-Me$_2$ (D groups): multitude of singlets at 0-0.5 ppm, 27 H.

Preparation of ^{14}C Polydiphenyldimethylsiloxane Oil

To a 50mL one-neck round-bottom flask equipped with a magnetic stir bar and a condenser with a nitrogen inlet, was added 0.03 grams (5 mCi) of ^{14}C D$_4$, 1.97 grams unlabeled D$_4$, 3.80 grams dodecamethylpentasiloxane (MD$_3$M), 4.20 grams octamethylcyclotetrasiloxane(D$_4^{Ph}$) and 100 µ of a solution of potassium trimethylsilanolate in methyl sulfoxide. The flask was heated to 170°C for 6 hours while stirring under nitrogen. After 6 hrs, the mixture was allowed to cool to room temperature and 30.2 mg of a solution of phosphoric acid in silicone fluid (silyl phospate)

was added and the mixture was stirred for a minimum of 30 minutes at room temperature. The resulting oil was then vacuum distilled at 250°C/0.03 mm Hg for 3 hrs to remove volatiles. The flask was cooled to room temperature and a clear fluid (a small amount of flocculent white precipitate is usually evident) was obtained (70% yield). Analysis of the resultant oil by ^{29}Si NMR revealed a dimethylsiloxy:diphenylsiloxy ratio of 46.7:53.3 (wt:wt) with 10.5 wt% trimethoxysiloxy endgroups.

Preparation of Silicone Coatings Containing ^{14}C Polydiphenyldimethylsiloxane Oil

Aluminum strips coated with epoxy were weighed and then coated with RTV11® containing 0.5 wt% dibutyltindilaurate catalyst and 10 wt% ^{14}C-labeled silicone oil. The strips were cured for 1 week and then weighed to determine the total weight of silicone topcoat (RTV + oil) per strip. The amount of ^{14}C-radiolabled oil was then calculated, assuming a uniform distribution of ^{14}C-oil throughout the network. The tin from the catalyst was then removed from the coupons by soaking them in water for several days. The tin rinse water was subsequently analyzed for total ^{14}C using liquid scintillation analysis to account for residual radiolabeled oil in the water.

Analysis of Radiolabeled Samples Containing ^{14}C Polydiphenyldimethylsiloxane Oil

One aluminum strip was removed each month and the amount of ^{14}C-labled oil in the RTV11® was measured by thermal oxidation, based on 3-5 samples. This process is described in a report by J. Carpenter (9). The total amount of oil in each coupon was calculated based on the total weight of the silicone topcoat for a specified aluminum coupon. In addition, the amount of ^{14}C in the water and sediment was determined by liquid scintillation analysis and thermal oxidation/ liquid scintillation analysis, respectively.

Experimental Design for ^{14}C Radiolabeled Study

The coated aluminum strips were suspended in fresh and salt water tanks containing fresh and marine water sediments, respectively (Figure 11). Fresh water sediment was obtained from the Scioto River (Columbus, OH) and marine sediment was obtained from Tampa Bay (FL) and the pH of the sediments was 7.5 and 7.9, respectively. Each three gallon fish tank contained 6 liters of distilled water and 305 grams of the appropriate sediment. To the marine tank, sea salt (0.5 cup/gallon of water) was added. The tanks were stored in the dark and the water was stirred to simulate movement of a boat in water.

Figure 11. Fish Tank Study Design
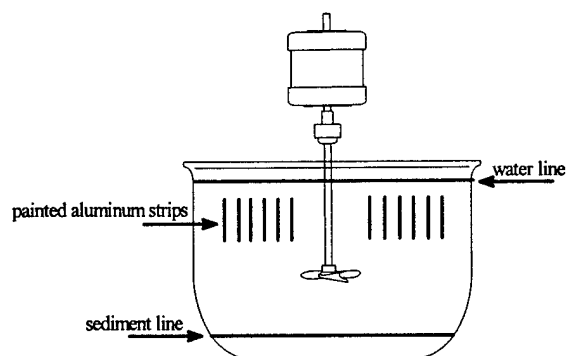
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